

FORM 1082

A

FORM PTO-1082

File Number: MAT-5870

THE ASSISTANT COMMISSIONER FOR PATENTS
Washington, D.C. 20231

Sir:

Transmitted herewith for filing is the patent application of
Inventor: Akiko Ishida, Ken Nishimura, Masahiko Ogawa, Nobuo Eda, Masaki Kitagawa, Tetsuhisa Sakai
For: LITHIUM SECONDARY BATTERY

Enclosed are:

- ☒ 7 sheets of drawing.
- ☐ An assignment of the invention to _____.
- ☒ A Declaration and Power of Attorney - UNEXECUTED.
- ☐ A verified statement to establish small entity status under 37 CFR 1.9 and 37 CFR 1.2
- ☒ Benefit of priority is claimed under 35 U.S.C. § 119.
- ☐ This application claims the benefit of U.S. Provisional Application No. _____ filed _____.

The filing fee has been calculated as shown below:

	(Col. 1)	(Col. 2)
FOR:	No. Filed	No. Extra
Basic Fee		
Total Claims	15-20=	0*
Indep Claims	3-3=	0*
<input type="checkbox"/> Multiple Dependent Claim Presented		

*If the difference in Col. 1 is less than zero, enter "0" in Col. 2.

SMALL ENTITY

Rate	Fee
	\$395
x \$11	\$
x \$41	\$
+ \$135	\$
TOTAL	\$

OTHER THAN A
SMALL ENTITY

OR	Rate	Fee
OR		\$ 790
OR	x \$22	\$
OR	x \$82	\$
OR	+ \$270	\$
OR	TOTAL	\$ 790

- ☐ Please charge my Deposit Account No. **18-0350** the amount of \$. A duplicate copy of this sheet is enclosed.
- ☒ A check in the amount of **\$790.00** to cover the filing fee is enclosed.
- ☒ The Assistant Commissioner for Patents is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 18-0350 . A duplicate copy of this sheet is enclosed.
 - ☒ Any additional filing fees required under 37 CFR 1.16.
 - ☒ Any patent application processing fees under 37 CFR 1.17.
- ☒ The Assistant Commissioner for Patents is hereby authorized to charge payment of the following fees during the pendency of this application or credit any overpayment to Deposit Account No. **18-0350** . A duplicate copy of this sheet is enclosed.
 - ☒ Any patent application processing fees under 37 CFR 1.17.
 - ☐ The issue fee set in 37 CFR 1.18 at or before mailing of the Notice of Allowance, pursuant to 37 CFR 1.311(b).
 - ☒ Any filing fees under 37 CFR 1.16 for presentation of extra claims.

RATNER AND PRESTIA
Suite 301,
One Westlakes, Berwyn
P. O. Box 980
Valley Forge, PA 19482-0980
(610) 407-0700

Respectfully submitted,

Allan Ratner, Reg. No. 19,717
Lawrence E. Ashery, Reg. No. 34,515

Is

EXPRESS MAIL Mailing Label Number: EL06328283US

Date of Deposit: March 12, 1998

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Lynn A. Pentz

LITHIUM SECONDARY BATTERY

Background of the Invention

The present invention relates to a lithium secondary battery, and more particularly to its electrode.

5 The lithium battery, in particular, the rechargeable lithium secondary battery is intensively researched and developed recently as a new secondary battery having high voltage and high energy density. In earlier studies, the lithium secondary battery using lithium metal in the negative electrode has been highly
10 expected as the battery of high energy density. However, when lithium metal is used in the negative electrode, dendric lithium formed at the time of charging is grown in the course of charging and discharging of battery, which leads to internal short circuit of battery or abnormal temperature rise of battery. Such safety
15 problems have not been solved yet.

 To solve these problems, instead of using lithium metal alone, it has been attempted to use an alloy of lithium metal with low melting metal such as aluminum, lead, indium, bismuth or cadmium, as the negative electrode. In these cases, however, as
20 charging and discharging are repeated, pulverized alloy penetrates through the separator to cause internal short circuit, and it is far from practical and the problems are not solved.

-2-

Recently, to solve the problems, using carbon in the negative electrode, the lithium secondary battery using transition metal compound containing lithium in the positive electrode is coming into the mainstream. In this battery system, since charging and discharging are done by occlusion and release of lithium ions into carbon in the negative electrode, dendrite is not formed by charging. Hence, the battery has an excellent cycle characteristic and is excellent in safety.

In the existing lithium secondary battery, as mentioned above, carbon is used as active substance in the negative electrode, and charging and discharging are effected by occlusion and release of lithium ions into carbon. When powder is used as active substance, required conditions of the negative electrode of the battery include, aside from the lithium ion occluding and releasing capacity of the carbon itself, the filling performance of filling the limited volume of the battery with how much carbon. In the lithium secondary battery, usually, a mixed paste of carbon and adhesive is applied on both sides or one side of thin metal films used as current collectors, and the obtained plates are dried and rolled to form electrodes. In the plates of high capacity type having such high filling performance, it is a technical problem to accelerate ion conduction in the limited gap existing in the active substance grain boundary. That is, by obtaining a smoother ion diffusion in the negative electrode, the internal resistance of the electrode is curtailed, and the lithium secondary battery of high capacity is realized also in high rate discharge.

Further researches are also made into the lithium secondary battery using polymer electrolyte, instead of organic electrolyte solution, as the electrolyte, and it is expected as a

-3-

lithium secondary battery of next generation featuring small size, light weight, and freedom of shape. However, the ion conductivity of polymer electrolyte is about 10^4 S/cm at most, which is about
55 two digits lower as compared with the organic electrolyte solution. Hence, to obtain a conductivity similar to that of the organic electrolyte solution, gel electrolyte impregnating organic electrolyte solution in polymer is used. The gel electrolyte is manufactured, for example, in the following method as disclosed in
60 Japanese Laid-open Patent No. 5-109310. A mixed solvent composed of an optical crosslinking polymer of polyethylene glycol diacrylate, an optical crosslinking monomer of trimethylol propane ethoxylated triacrylate, an electrolyte solution solvent of propylene carbonate or polyethylene oxide, an electrolyte salt of LiCF_3SO_3 ,
65 and others is applied on a flat plate, and it is irradiated with electron beams to polymerize and cure the monomer, so that a transparent and soft film of gel electrolyte is obtained. In the gel electrolyte, since ion conduction is mostly conducted through electrolyte solution phase, a high ion conductivity of about 3×10^3
70 S/cm can be obtained at room temperature.

In the lithium polymer secondary battery, as the substitute for separator used in the ordinary battery system, the polymer electrolyte is bonded with positive electrode and negative electrode, and the battery is composed. In the case of an ordinary
75 secondary lithium battery using organic electrolyte solution, the positive electrode is composed of active substance, conductive agent and bonding agent, and electrolyte solution is impregnated, so that a favorable electrochemical interface with the active substance is obtained. However, the gel electrolyte which is a
80 solid form lacks fluidity, and hardly permeates into the inside of

-4-

the electrode. Accordingly, a compound electrode containing polymer electrolyte preliminarily in the electrode is formed, and it is bonded with the polymer electrolyte to fabricate the battery.

However, the conventional gel polymer electrolyte described above is characterized by containing organic electrolyte solution, and although the polymer electrolyte shows a high ion conductivity, it has not reached the level of organic electrolyte solution yet in terms of characteristics. When the battery is composed by introducing this polymer electrolyte into the electrode, owing to the low ion conductivity of the electrolyte itself, the internal resistance of the electrode is increased, and the charging and discharging capacity of the battery is extremely spoiled. Hence, to fabricate the battery of high capacity type, it is required to enhance the ion conductivity of polymer electrolyte in the electrode, and compose a battery of low internal resistance.

Summary of the Invention

A lithium secondary battery is composed of a positive electrode, a negative electrode, and an electrolyte, and at least one of the positive electrode and negative electrode contains ceramic not responsible for charging and discharging reaction of the battery.

According to the invention, by mixing ceramic particles in the electrode, either positive electrode or negative electrode, the ion conductivity is enhanced, and the internal resistance of the electrode is lowered. By combining such positive and negative electrode for lithium battery and the electrolyte, a lithium secondary battery of high capacity particularly in high rate

discharge is obtained.

At the same time, by adding ceramic particles in the plates, the plate strength is increased, and the lithium secondary battery excellent in cycle life characteristic can be manufactured.

As disclosed in Japanese Laid-open Patent No. 8-509100, an inorganic filler such as alumina or silanated fumed silica is added in the electrolyte, and the mechanical strength of the separator film is increased, and the electrolyte absorption level is heightened, but its constitution is different from the present invention in which ceramic particles are contained in the electrode, and it is also different in purpose, action and effect from the present invention which is intended to enhance the ion conductivity and lower the internal resistance of the battery.

In Japanese Laid-open Patent No. 7-235293, it is claimed that the electron conductivity is enhanced by using the active substance, having a compound mainly composed of semimetal belonging to group IV-B or V-B of periodic table as the dopant. It is the reformation of the active substance itself of the negative electrode, and is different from the present invention in its purpose and means. Besides, by adding Al_2O_3 , In_2O_3 , SnO_2 , ZnO in the positive electrode in Japanese Laid-open Patent No. 7-153495, or mixing BaO , MgO , CaO in the positive electrode in Japanese Laid-open Patent No. 7-153496, it is reported that the stability of the positive electrode active substance having lithium ions de-doped in charged state is enhanced, thereby improving the capacity deterioration in the course of charging and discharging cycles. It is only intended to stabilize the positive electrode active substance by adding to the electrode, which is radically different

-6-

from the constitution, action and purpose of the present invention in which additives are added to the negative electrode of the lithium ion battery.

Brief Description of the Drawings

140 Fig. 1 is a longitudinal sectional view of a power generating element of a lithium polymer secondary battery of an example of the invention.

145 Fig. 2 is a longitudinal sectional view of a power generating element of a lithium polymer secondary battery in other embodiment of the invention.

Fig. 3 is a diagram showing discharge capacity for discharge current density in a lithium polymer secondary battery.

Fig. 4 is a diagram showing discharge capacity for discharge current density in a lithium polymer secondary battery.

150 Fig. 5 is a diagram showing discharge capacity to additive rate of Al_2O_3 particles mixed in the positive electrode.

Fig. 6 is a diagram showing discharge capacity to particle size of Al_2O_3 particles mixed in the positive electrode.

155 Fig. 7 is a longitudinal sectional view of a lithium ion secondary battery using electrodes of the invention.

Fig. 8 is a diagram showing a discharge curve of lithium secondary battery.

Fig. 9 is a diagram showing rate characteristic of lithium secondary battery.

-7-

160 Fig. 10 is a longitudinal sectional view of a power generating element of a lithium polymer secondary battery of an example of the invention.

Fig. 11 is a diagram showing discharge capacity for discharge rate in a lithium polymer secondary battery.

165 Detailed Description of the Preferred Embodiments

The invention relates to a lithium secondary battery using electrodes containing ceramic particles in at least one of positive electrode and negative electrode. By containing ceramics in the electrode, the ion conductivity is enhanced, so that a lithium
170 secondary battery of low internal resistance is obtained. As a result, the lithium secondary battery capable of charging and discharging at high rate and higher in capacity is obtained.

The ceramic is at least one selected from the group consisting of Al_2O_3 , SiO_2 , ZrO_2 , MgO and Na_2O . The ceramic is
175 used in particles, and the particle size should be 10 microns or less. For transmission of lithium ions, the surface porous portion of ceramic particles, more specifically the porous volume is responsible, and by using ceramic particles of small particle size and wide surface area, more effective ion diffusion capacity is
180 obtained.

The ceramic content is 0.01 to 20 parts by weight in 100 parts by weight of active substance. By the presence of ceramic particles, the ion conductivity of electrode is enhanced, but its effect appears at 0.01 parts by weight or more, and if too
185 much ceramic is present in the electrode, the electrolyte volume as the ion transmission route decreases suddenly, and therefore the

-8-

ceramic to be mixed in the electrode is appropriately 20 wt. % or less. More preferably, it may be 10 wt. % or less, so that a lithium secondary battery of high capacity is obtained.

190 The invention relates to a lithium secondary battery containing polymer electrolyte in at least one of positive electrode and negative electrode. The solid electrolyte lacks fluidity, and hence hardly permeates into the electrode, and therefore by preliminarily containing electrolyte in the electrode to obtain a
195 compound electrode, so that the ion conductivity is enhanced.

 The polymer electrolyte is a gel polymer electrolyte composed of polymer and organic electrolyte solution dissolving lithium salt. As a result, the ion conductivity of electrolyte is enhanced.

200 Moreover, ceramic is contained in the polymer electrolyte. As a result, the ion conductivity in the polymer electrolyte is enhanced, and a lithium secondary battery of lower internal resistance is obtained.

 The ceramic in the electrolyte is at least one kind
205 selected from the group consisting of Al_2O_3 , SiO_2 , ZrO_2 , MgO and Na_2O .

 The ceramic particles should be 10 microns or less in particle size.

Example 1

210 Using a polymer electrolyte compound positive electrode mixing Al_2O_3 particles, a lithium polymer secondary battery of the invention was fabricated.

-9-

Fig. 1 is a longitudinal sectional view of a lithium polymer secondary battery of the invention. In the diagram, reference numeral 1 is a lithium metal negative electrode, and 3 is a compound positive electrode containing polymer electrolyte mixing Al_2O_3 particles. Besides, reference numeral 2 is a gel polymer electrolyte layer, and 4 is an aluminum-made current collecting foil of positive electrode.

The polymer electrolyte compound positive electrode 3 mixing Al_2O_3 particles was fabricated in the following manner. First, as monomer, Al_2O_3 particles with particle size of 0.5 micron were added by 10 parts by weight to 20 parts by weight of polyethylene glycol diacrylate, and stirred. Adding 0.5 part by weight of thermal polymerization initiator and 70 parts by weight of nonaqueous electrolyte solution, the mixture was stirred by a ball mill, and a thermal polymerizable polymer electrolyte cured solution uniformly dispersing Al_2O_3 particles was obtained. In succession, to 100 parts by weight of V_6O_{13} active substance, 6 parts by weight of acetylene black and 50 parts by weight of the thermal polymerizable polymer electrolyte cured solution were injected and kneaded. This paste of positive electrode compound was applied on an aluminum foil which is a positive electrode current collector, and by heating for 1 hour at 80, the monomer was polymerized and cured, and the polymer electrolyte compound positive electrode 3 mixing 5 parts by weight of Al_2O_3 particles in 100 parts by weight of active substance was obtained.

Consequently, the gel polymer electrolyte layer 2 was fabricated in the following manner. First, as the monomer, mixing and stirring 0.1 part by weight of optical polymerization initiator and 70 parts by weight of nonaqueous electrolyte solution in 20

-10-

parts by weight of polyethylene glycol diacrylate, an optical polymerizable polymer electrolyte curing solution was obtained. It was applied in a thickness of 50 microns, and an ultraviolet ray
245 with maximum output wavelength of 365 nm was emitted for 3 minutes. As a result, the monomer was polymerized and cured, and a gel polymer electrolyte layer 2 containing nonaqueous electrolyte solution was obtained.

This gel polymer electrolyte layer 2 was bonded and
250 laminated with lithium metal negative electrode 1 and polymer electrolyte compound positive electrode 3, and the coin type lithium polymer secondary battery of the invention was composed.

Herein, the thermal polymerization initiator was azoisobutyronitrile, the optical polymerization initiator was benzyl
255 dimethyl ketal, and the nonaqueous electrolyte solution was an equally mixed solvent of propylene carbonate and ethylene carbonate by 50:50 by volume, dissolving 1 mol/liter of LiPF_6 as a solute.

Example 2

260 The coin type lithium polymer secondary battery of the invention was composed in the same manner as in example 1, except that the particle size of Al_2O_3 particles to be mixed in the polymer electrolyte compound positive electrode 3 was fixed at 0.5 micron, and that the additive rate in 100 parts by weight of active
265 substance was 5, 10, 20 and 30 parts by weight.

Example 3

The coin type lithium polymer secondary battery of the

-11-

invention was composed in the same manner as in example 1, except that the additive rate of Al_2O_3 particles mixed in the polymer electrolyte compound positive electrode 3 was fixed at 5 parts by weight in 100 parts by weight of active substance, and that the particle size of Al_2O_3 particles was 0.5, 1.0, 10 and 20 microns.

Example 4

The coin type lithium polymer secondary battery of the invention was composed in the same manner as in example 1, except that Al_2O_3 particles were contained in the gel polymer electrolyte layer.

The gel polymer electrolyte layer containing Al_2O_3 particles was manufactured in the following manner. First, as monomer, 10 parts by weight of Al_2O_3 particles with particle size of 0.5 micron were added and stirred in 20 parts by weight of polyethylene glycol diacrylate. Adding 0.1 part by weight of optical polymerization initiator and 70 parts by weight of nonaqueous electrolyte solution, the mixture was stirred by a ball mill, and an optical polymerizable polymer electrolyte cured solution uniformly dispersing Al_2O_3 particles was obtained. It was applied in a thickness of 50 microns, and an ultraviolet ray with maximum output wavelength of 365 nm was emitted for 3 minutes. As a result, the monomer was polymerized and cured, and gel polymer electrolyte layer containing nonaqueous electrolyte solution and dispersing Al_2O_3 particles was obtained.

This gel polymer electrolyte layer dispersing Al_2O_3 particles was bonded and laminated with lithium metal negative

-12-

295 electrode 1 and polymer electrolyte compound positive electrode 3
same as in example 1, and the coin type lithium polymer secondary
battery of the invention was composed.

Example 5

300 A lithium polymer secondary battery of the invention
was composed by using a polymer electrolyte compound negative
electrode mixing Al_2O_3 particles.

Fig. 2 shows a longitudinal sectional view of a lithium
polymer secondary battery in other embodiment of the invention.
In the diagram, reference numeral 5 is a negative electrode current
305 collector, and a polymer electrolyte compound negative electrode 6
mixing Al_2O_3 particles is applied. It is laminated with a polymer
electrolyte compound positive electrode 8 applied on a positive
electrode current collector 9 with a gel polymer electrolyte 7
inbetween.

310 The polymer electrolyte compound negative electrode 6
mixing Al_2O_3 particles was manufactured in the following manner.
First, to the monomer of 20 parts by weight of polyethylene glycol
diacrylate, Al_2O_3 particles with particle size of 0.5 micron was
added and stirred by 10 parts by weight. Further adding 0.5 part
315 by weight of thermal polymerization initiator and 70 parts by
weight of nonaqueous electrolyte solution, the mixture was stirred
by a ball mill, and a thermal polymerizable polymer electrolyte
cured solution uniformly dispersing Al_2O_3 particles was obtained.
In succession, as negative electrode active substance, to 90 parts
320 by weight of graphite powder with particle size of 6 microns,
polyvinylidene fluoride was mixed by 10 parts by weight as binder,

-13-

and the thermal polymerizable polymer electrolyte cured solution was injected by 50 parts by weight and kneaded. This paste of negative electrode compound was applied on a copper foil of the negative electrode current collector 5, and dried at reduced pressure at 150, and blanked, and the polymer electrolyte compound negative electrode 6 mixing 5 parts by weight of Al_2O_3 particles in 100 parts by weight of active substance was obtained.

The polymer electrolyte compound positive electrode 8 was fabricated in the following manner. First, to the monomer of 20 parts by weight of polyethylene glycol diacrylate, 0.5 part by weight of thermal polymerization initiator and 70 parts by weight of nonaqueous electrolyte solution were added and stirred, and a thermal polymerizable polymer electrolyte cured solution was obtained. In succession, to 100 parts by weight of LiCoO_2 as positive electrode active substance, 3 parts by weight of acetylene black and 50 parts by weight of the thermal polymerizable polymer electrolyte curing solution were injected and kneaded. This paste of positive electrode compound was applied on an aluminum foil of the positive electrode current collector 9, and by heating for 1 hour at 80, the monomer was polymerized and cured, and the polymer electrolyte compound positive electrode 8 was obtained.

The gel polymer electrolyte layer 7 was fabricated in the same manner as in example 1. This gel polymer electrolyte layer 7 was bonded and laminated with the polymer electrolyte compound negative electrode 6 and polymer electrolyte compound positive electrode 8, and the coin type lithium polymer secondary battery of the invention was composed.

Herein, the thermal polymerization initiator was

350 azoisobutyronitrile, the optical polymerization initiator was benzyl dimethyl ketal, and the nonaqueous electrolyte solution was a mixed solvent of ethylene carbonate and ethyl methyl carbonate by 25:75 by volume, dissolving 1.5 mol/liter of LiPF_6 as a solute.

Example 6

355 The coin type lithium polymer secondary battery of the invention was composed in the same manner as in example 5, except that Al_2O_3 particles were contained in the gel polymer electrolyte layer.

360 The gel polymer electrolyte containing Al_2O_3 particles was manufactured in the same manner as in example 4.

365 The gel polymer electrolyte layer containing Al_2O_3 particles was bonded and laminated with the polymer electrolyte compound negative electrode 6 and polymer electrolyte compound positive electrode 8, and the coin type lithium polymer secondary battery of the invention was composed.

Example 7

A lithium polymer secondary battery of the invention was composed by using the polymer electrolyte compound negative electrode and positive electrode mixing Al_2O_3 particles.

370 The coin type lithium polymer secondary battery of the invention was composed in the same manner as in example 6, except that Al_2O_3 particles were contained in the polymer electrolyte compound positive electrode.

The polymer electrolyte compound positive electrode

-15-

375 mixing Al_2O_3 particles was manufactured in the following manner.
First, to the monomer of 20 parts by weight of polyethylene glycol
diacrylate, Al_2O_3 particles with particle size of 0.5 micron was
added and stirred by 10 parts by weight. Further adding 0.5 part
by weight of thermal polymerization initiator and 70 parts by
380 weight of nonaqueous electrolyte solution, the mixture was stirred,
and a thermal polymerizable polymer electrolyte cured solution was
obtained. In succession, as positive electrode active substance, to
100 parts by weight of LiCoO_2 , 3 parts by weight of acetylene
black and 50 parts by weight of the thermal polymerizable polymer
385 electrolyte cured solution were injected and kneaded. This paste of
positive electrode compound was applied on an aluminum foil, and
by heating for 1 hour at 80, the monomer was polymerized and
cured, and the polymer electrolyte compound positive electrode
mixing Al_2O_3 particles was obtained.

390 The polymer electrolyte compound positive electrode
and polymer electrolyte compound negative electrode dispersing
 Al_2O_3 particles were bonded and laminated with the gel polymer
electrolyte layer 7, and the coin type lithium polymer secondary
battery of the invention was composed.

395 Example 8

A cylindrical lithium ion secondary battery of the
invention was composed by using a negative electrode mixing
alumina (Al_2O_3) particles.

Fig. 7 shows a longitudinal sectional view of a
400 cylindrical lithium ion secondary battery of the invention. In the
diagram, reference numeral 11 is a negative electrode mixing Al_2O_3

-16-

particles, and it was manufactured in the following manner. First, as negative electrode active substance, to 90 parts by weight of graphite powder, 10 parts by weight of polyvinylidene fluoride as binder and N-methyl-2-pyrrolidone as solvent were mixed, and a specified amount of Al_2O_3 particles with specified particle size were mixed and kneaded, and a paste was prepared. A specified amount of this compound was applied on both sides of a copper foil as negative electrode current collector, and dried, rolled, and cut to a specified size, and a negative electrode 11 for lithium secondary battery was fabricated. Reference numeral 13 is a positive electrode, and it was manufactured in the following manner. To 100 parts by weight of LiCoO_2 positive electrode active substance, 3 parts by weight of acetylene black and 9 parts by weight of aqueous dispersion of polytetrafluoroethylene were added and kneaded to prepare a paste. It was applied on both sides of an aluminum foil as positive electrode current collector, and dried and rolled, and cut to a specified size, and a positive electrode 13 for lithium ion secondary battery was obtained. Reference numeral 15 is a separator composed of a polyethylene microporous film, and it is interposed between the positive electrode 13 and negative electrode 11, and a spiral plate group is composed on the whole.

At upper and lower ends of the plate group, an upper insulator 16 and a lower insulator 17 of polypropylene are disposed, and the assembly is inserted into a nickel plated iron case 18. A positive electrode lead plate 14 is spot-welded to a titanium sealing plate 20 and a negative electrode lead plate 12, to the bottom of the case 18, and a specified amount of electrolyte solution is injected into the case, and the battery is sealed with the

-17-

sealing plate 20 through a gasket 19, and a cylindrical lithium secondary battery of the invention is obtained. The battery measures 14 mm in diameter and 50 mm in height. Reference numeral 21 is a positive electrode terminal of the battery, and the battery case 18 serves as the negative electrode terminal. Herein, the electrolyte solution is a nonaqueous electrolyte solution dissolving 1.5 mol/liter of LiPF_6 in a mixed solvent of ethylene carbonate and ethyl methyl carbonate at 25:75 by volume.

Example 9

The cylindrical lithium ion secondary battery of the invention was composed in the same manner as in example 8, except that the particle size of Al_2O_3 particles to be mixed in the negative electrode was fixed at 0.5 micron, and that the additive rate in 90 parts by weight of graphite and 10 parts by weight of binder was 0.01, 5, 10, 20 and 30 parts by weight.

Example 10

The cylindrical lithium ion secondary battery of the invention was composed in the same manner as in example 8, except that the additive rate of Al_2O_3 particles mixed in the negative electrode was fixed at 5 parts by weight in 90 parts by weight of graphite and 10 parts by weight of binder, and that the particle size of Al_2O_3 particles was 0.5, 1.0, 10 and 20 microns.

Comparative example 1

The coin type lithium polymer secondary battery of the invention was composed in the same manner as in example 1, except that Al_2O_3 particles were not contained in the polymer

electrolyte compound positive electrode.

Comparative example 2

The coin type lithium polymer secondary battery of the
460 invention was composed in the same manner as in example 5,
except that Al_2O_3 particles were not contained in the polymer
electrolyte compound negative electrode.

Comparative example 3

The cylindrical lithium ion secondary battery of the
465 invention was composed in the same manner as in example 8,
except that Al_2O_3 particles were not contained in the negative
electrode.

The characteristics of these batteries in examples 1 to
10 and comparative examples 1-3 were evaluated. The results are
470 shown in Fig. 3 to Fig. 6, Fig. 8, and Fig. 9.

In Fig. 3, the current-capacity characteristic of the coin
type lithium polymer secondary batteries obtained in example 1,
example 4, and comparative example 1 are expressed as the
discharge capacity to the discharge current density. In the test, the
475 battery was charged at a constant current of 0.5 mA/cm^2 , and
discharged at a current density of 0.5 to 6.0 mA/cm^2 , in a voltage
range of 1.8 to 3.3 V , at 20°C . As a result, as compared with the
battery of comparative example 1, the battery of example 1 mixing
 Al_2O_3 particles in the positive electrode of the invention was
480 extremely enhanced in the discharge capacity at the discharge
current density of 1 mA/cm^2 or more. The battery in example 4
mixing Al_2O_3 fine particles also in the gel polymer electrolyte layer

was further improved in the discharge capacity as compared with the battery of example 1.

485 In Fig. 4, the current-capacity characteristic of the coin type lithium polymer secondary batteries obtained in example 5 to example 7, and comparative example 2 are expressed as the discharge capacity to the discharge current density.

490 In the test, the battery was charged at a constant current of 0.5 mA/cm², and discharged at a current density of 0.5 to 6.0 mA/cm², in a voltage range of 3.0 to 4.2 V, at 20. As a result, as compared with the battery of comparative example 2, the battery of example 5 mixing Al₂O₃ particles in the negative electrode of the invention was enhanced in the capacity in a high discharge current
495 density region. The battery in example 6 mixing Al₂O₃ particles also in the polymer electrolyte layer was further improved in the discharge capacity as compared with the battery of example 5. Moreover, a high capacity was recorded in the battery of example 7 mixing Al₂O₃ particles in the positive electrode, negative
500 electrode and polymer electrolyte. In the battery of comparative example 2, at discharge of 6.0 mA/cm², the capacity is about 48% of that at discharge of 0.5 mA/cm², whereas in the battery of example 6, a high capacity maintenance rate of 77% was obtained.

505 Fig. 5 is a diagram showing the discharge capacity in terms of the additive amount of Al₂O₃ particles mixed in the positive electrode of the coin type lithium polymer secondary battery using the polymer electrolyte compound positive electrode obtained in example 2. In the test, the battery was discharged at a current density of 3.0 mA/cm², and charged at 0.5 mA/cm², at 20.
510 As a result, the discharge capacity increased along with the

-20-

addition of Al_2O_3 particles, showing the maximum value of 2.6 mAh at 5 wt. %. However, at the additive rate of 20 wt. % or more, to the contrary, the discharge capacity decreased as compared with the battery without additive.

Fig. 6 is a diagram showing the discharge capacity in terms of the particle size of Al_2O_3 particles mixed in the positive electrode of the coin type lithium polymer secondary battery using the polymer electrolyte compound positive electrode obtained in example 3. In the test, the battery was discharged at a current density of 3.0 mA/cm², and charged at 0.5 mA/cm², at 20. As a result, the discharge capacity increased along with the decrease of particle size, and a high capacity over 2.0 mAh was obtained at particle size of 10 microns or less.

As a result of measurement of X-ray diffraction of the positive electrode and negative electrode after charging and discharging, there was no difference in the peak of Al_2O_3 . Hence, it is estimated that Al_2O_3 is not related to charging and discharging.

Fig. 8 shows the discharge curve at the tenth cycle of the lithium secondary batteries obtained in example 8 and comparative example 3. In the test, the battery was charged at a constant current of 100 mA and discharged at 500 mA, the charge end voltage was 4.2 V and discharge end voltage was 3.0 V, and the cycle test was conducted in the environments at 20. As a result, the battery of comparative example 3 had a capacity of 405 mAh, and the battery of the invention in example 8 mixing Al_2O_3 particles in the negative electrode was increased in capacity by 6% to 430 mAh. This is because the internal resistance of the battery

is low, the voltage drop in discharge is small, and a high voltage is
540 maintained.

In Fig. 9, the current-capacity characteristics of the lithium secondary batteries obtained in example 8 and comparative example 3 are expressed as the discharge capacity to the discharge current. In the test, the battery was charged at a constant current
545 of 100 mA, and discharged at 100, 250, 500, and 1000 mA. In low rate discharge at 100 mA, in the battery of example 8 mixing Al_2O_3 particles in the negative electrode, the capacity was decreased by 4% as compared with the battery of comparative example 3 due to decline of quantity of active substance, but in high rate discharge
550 at 250 mA and higher, the capacity was improved. Besides, the battery of comparative example 3, in discharge at 1000 mA, the capacity was about 83% that in discharge at 100 mA, while a high capacity maintenance rate of 90% was observed in the battery of example 8.

555 In the test, the battery of example 9 was charged at 100 mA and discharged at 500 mA at 20. As a result, the discharge capacity increased together with the addition of Al_2O_3 particles, showing the maximum value of 430 mAh at 5 wt.%. However, at 20 wt.% or more, to the contrary, the discharge capacity decreased
560 due to addition. This seems because quantities of ceramic fine particles are present in the electrode and the electrolyte volume as the ion transmission route is decreased suddenly. Hence, ceramic fine particles to be mixed in the electrode should be preferably 20 wt.% or less, and a lithium secondary battery of high capacity is
565 obtained at this time.

The discharge capacity in terms of particle size of Al_2O_3

-22-

particles mixed in the negative electrode of the lithium secondary battery obtained in example 10 was improved as the particle size of mixed Al_2O_2 particles decreased, and a high capacity of over 420 mAh was obtained at particle size of 10 microns or less. This is considered because the surface porous portion of ceramic particles, more specifically, the porous volume is closely related to transmission of lithium ions, and an effective ion diffusion is achieved by using ceramic particles of small particle size and wide surface area.

In both charge and discharge states, the X-ray diffraction analysis of the negative electrode after charging and discharging disclosed no difference in Al_2O_3 peaks. Hence, Al_2O_3 is not considered to be related to occlusion and release of lithium.

Moreover, the cycle characteristics of the lithium secondary batteries of example 8 and comparative example 3 were studied. The battery test was conducted at the discharge current of 500 mA, upper limit end voltage of 4.2 V, lower limit end voltage of 3.0 V, and in the environment of 20. Results of discharge capacity at 0, 100, and 500 cycles are shown in Table 1.

Table 1

	Initial capacity (mAh)	Capacity after 100 cycles (mAh)	Capacity after 500 cycles (mAh)
Example 8	430	414	404
Comparative example 3	405	376	365

As clear from Table 1, in the battery of comparative example 3, the capacity decrease to 93% of initial capacity in 100 cycles, and 90% in 500 cycles, but the battery of example 8 of the invention maintained 94% of initial capacity after 500 cycles. The battery was decomposed after 500 cycles, and the negative electrode was observed, and the plate of example 8 containing Al_2O_3 was less in dropout of negative electrode compound and higher in strength as compared with the plate of comparative example 3 without additive.

Example 11

A lithium polymer secondary battery of the invention was composed by using a polymer electrolyte compound positive electrode mixing Al_2O_3 particles.

Fig. 10 is a longitudinal sectional view of the lithium polymer secondary battery of the invention. In the diagram, a positive plate 31 is a laminated structure of a positive electrode active substance layer 31a and a positive electrode current collector 31b. A negative plate 32 is similarly a laminated

605 structure of a negative electrode active substance layer 32a and a
negative electrode current collector 32b. A polymer electrolyte 33
is placed between the positive plate and negative plate, and is
integrated with the positive plate and negative plate by hot melting
or casting method.

610 The positive electrode current collector 31b is a
punching metal or lath metal composed of aluminum metal or
conductive material coated with aluminum, and a mixture of
conductive carbon material such as acetylene black, Ketchen Black,
or carbon fiber, and a binder such as polyvinylidene fluoride is
615 bonded to the surface.

The negative electrode current collector 32b is a
punching metal or lath metal composed of nickel metal or
conductive material coated with copper or nickel, and a mixture of
conductive carbon material such as acetylene black, Ketchen Black,
620 or carbon fiber, and a binder such as polyvinylidene fluoride is
bonded to the surface.

In the method of binding the conductive carbon material
to the current collector, for example, acetylene black is dispersed
in N-methyl pyrrolidone solution of polyvinylidene fluoride, and
625 this solution is directly applied on the current collector, and the
solvent, N-methyl pyrrolidone, is dried and removed.

The positive electrode active substance layer 31a and
negative electrode active substance layer 32a are fabricated by
applying a paste composed of active substance, conductive
630 material, and polymer solution on a glass plate, and drying and
removing the solvent. The positive electrode active substance

-25-

layer 31a, positive electrode current collector 31b, negative electrode active substance layer 32a, and negative electrode current collector 32b are melted by heat roller to prepare the positive plate 31 and negative plate 32, and the polymer electrolyte 33 is laminated with the positive plate 31 and negative plate 32, and melted by heat roller to prepare the laminate electrode 34.

The laminate electrode 34 is inserted into the laminate sheet housing, and from the opening of the housing, an electrolyte solution dissolving 1 mol/liter of lithium phosphate hexafluoride in a mixture of ethylene carbonate and ethyl methyl carbonate at 1:3 by volume is poured in. After pouring the solution, the inside of the housing is evacuated and heated to impregnate the electrolyte solution sufficiently in the laminate electrode, and is then returned to atmospheric pressure, and the opening of the housing is sealed by heat seal, and the organic electrolyte battery of the invention is obtained.

A lithium polymer secondary battery of the invention using polymer electrolyte compound positive electrode mixing Al_2O_3 particles was prepared in the following procedure.

In 160 g of acetone, 45 g of copolymer of vinylidene fluoride and propylene hexafluoride (hereinafter called P(VDF-HFP) (ratio of propylene hexafluoride 12% by weight) is dissolved, and 45 g of di-n-butyl phthalate (DBP) is added to prepare a mixed solution. This solution is applied on a glass plate in a deposition thickness of 0.5 mm, and acetone is dried and removed, and a polymer electrolyte sheet of 0.08 mm in thickness and 40 mm 70 mm in size is prepared.

-26-

As the positive electrode sheet, 90 g of P(VDF-HFP) is
660 dissolved in 1300 g of acetone, and 1000 g of lithium cobaltate, 60
g of acetylene black, 135 g of DBP, and 100 g of Al_2O_3 particles
with particle size of 0.5 micron are mixed and the prepared paste
is applied on a glass plate in a deposition thickness of 0.9 mm, and
acetone is dried and removed, and a sheet of 0.3mm in thickness
665 and 30 mm 60 mm in size is obtained.

As the negative electrode sheet, 45 g of P(VDF-HFP) is
dissolved in 300 g of acetone, and 260 g of spherical graphite
(Osaka Gas) composed of carbon mesophase spheres transformed
into carbon and graphite, 20 g of vapor phase growth carbon fiber
670 transformed into graphite (VGCF) (Osaka Gas), and 65 g of DBP
are mixed, and the prepared paste is applied on a glass plate in a
deposition thickness of 1.2 mm, and acetone is dried and removed,
and a sheet of 0.35 mm in thickness and 30 mm 60 mm in size is
obtained.

675 The mixture of conductive carbon material and binder to
be applied on the current collector is prepared by dispersing and
mixing 30 g of acetylene black and N-methyl pyrrolidone solution
(12 wt. %) of polyvinylidene fluoride. This mixture is applied on a
lath metal of aluminum and copper of 0.06 mm in thickness, and by
680 drying and removing N-methyl pyrrolidone at temperature of 80 or
higher, the current collector is prepared.

The laminated structure of the positive electrode sheet
and current collector of aluminum is laminated with
polytetrafluoroethylene sheet (PTFE, 0.05 mm thick), and heated
685 and pressurized by passing through two rollers heated at 150 to
melt. The PTFE is used to prevent the active substance layer from

-27-

adhering to the rollers, and other material such as copper foil or aluminum foil may be used.

In the same manner, the negative plate is prepared by
690 using the negative electrode sheet and copper current collector.

Finally, the polymer electrolyte is laminated with the positive plate and negative plate, and heated and pressurized by two rollers heated at 120 to melt and integrate, thereby composing a composition battery. The integrated composition battery is
695 immersed in diethyl ether, and DBP is extracted and removed, and dried in vacuum at 50.

Finally, in the integrated composition battery, an electrolyte solution dissolving 1.5 mol/liter of lithium phosphate hexafluoride in a mixture of ethylene carbonate and ethyl methyl
700 carbonate at 1:3 by volume is poured. After pouring the solution, the inside of the housing is evacuated and heated to impregnate the electrolyte solution sufficiently in the laminate electrode, and is returned to atmospheric pressure, and the opening of the housing is sealed by heat seal, and the lithium polymer secondary battery of
705 the invention is obtained.

Example 12

A lithium polymer secondary battery of the invention was prepared in the same manner as in example 11, except that Al_2O_3 particles with particle size of 0.5 micron same as used in
710 example 11 were contained in the polymer electrolyte.

The polymer electrolyte mixing Al_2O_3 particles was prepared in the following manner.

-28-

In 160 g of acetone, 30 g of copolymer of vinylidene fluoride and propylene hexafluoride (hereinafter called P(VDF-HFP) (ratio of propylene hexafluoride 12% by weight) is dissolved, and 30 g of di-n-butyl phthalate (DBP) is added, and Al_2O_3 particles with particle size of 0.5 microns are added to this mixed solution. This solution is applied on a glass plate in a deposition thickness of 0.5 mm, and acetone is dried and removed, and a polymer electrolyte sheet of 0.08 mm in thickness and 40 mm 70 mm in size is prepared.

Comparative example 4

A lithium polymer secondary battery of comparative example was prepared in the same manner as in example 11, except that Al_2O_3 particles are not contained in the polymer electrolyte compound positive electrode.

The characteristics were evaluated in the batteries thus prepared in examples 11 and 12 and comparative example 4. Fig. 11 shows the discharge capacity in terms of the discharge rate plotted on the axis of abscissas. The discharge end voltage was 3 V. As a result, as compared with the battery not containing Al_2O_3 particles in comparative example, the battery of example 11 mixing Al_2O_3 particles in the positive electrode of the invention was extremely enhanced in the discharge capacity at the high discharge rate. Moreover, in the battery of example 12 mixing Al_2O_3 particles also in the polymer electrolyte, the discharge capacity was further enhanced as compared with the battery of example 11.

In the embodiments, LiPF_6 was used as the solute of nonaqueous electrolyte solution, but it may be replaced by other

-29-

740 lithium salt, such as LiCF_3SO_3 , LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)$, LiAsF_6 , or LiBF_4 .

Also in the embodiments, as the solvent of the nonaqueous electrolyte solution, a mixed solvent of propylene carbonate and ethylene carbonate, and a mixed solvent of ethylene carbonate and ethyl methyl carbonate were used, but other organic
745 solvents or their mixed solvents may be used.

As the positive electrode active substance of the embodiments, V_6O_{13} and LiCoO_2 were used, but they may be also replaced by MnO_2 , $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ($0 < x < 0.1$), LiNiO_2 , Li_xMnO_2 ($0 < x < 0.5$),
750 and other lithium transition metal composite compound.

Lithium metal and graphite powder were used in the negative electrode of the embodiments, but other carbon material, metal oxide, metal nitride, and other metal compounds may be also used.

755 In the embodiments, as ceramic fine particles, Al_2O_3 were used, but same effects were obtained by using SiO_2 , ZrO_2 , MgO , and Na_2O .

Ceramic particles were used in the embodiments, but the shape of particles is not limited to granular form, but same effects
760 were obtained in fibrous ceramic particles having a wide specific surface area.

Thus, according to the invention, by mixing ceramic particles in the positive and/or negative electrode, the electrode capacity was enhanced particularly in high rate discharge. By
765 combining the positive and negative electrodes for lithium battery

-30-

and the electrolyte, the lithium secondary battery of high capacity was obtained.

2025 RELEASE UNDER E.O. 14176

Claims

1 1. A lithium polymer secondary battery comprising a
2 positive electrode, a negative electrode, and a polymer electrolyte,
3 further containing ceramic not relating to charge and discharge
4 reaction of battery in at least one of positive electrode and
5 negative electrode.

1 2. A lithium polymer secondary battery of claim 1,
2 wherein the ceramic is at least one type selected from the group
3 consisting of Al_2O_3 , SiO_2 , ZrO_2 , MgO , and Na_2O .

1 3. A lithium polymer secondary battery of claim 1,
2 wherein the ceramic is granular, and the particle size is 10 microns
3 or less.

1 4. A lithium polymer secondary battery of claim 1,
2 wherein the content of the ceramic is 0.01 to 20 parts by weight in
3 100 parts by weight of the active substance.

1 5. A lithium polymer secondary battery of claim 1,
2 wherein a polymer electrolyte is contained in at least one of the
3 positive electrode and negative electrode.

1 6. A lithium polymer secondary battery of claim 1,
2 wherein the polymer electrolyte is a gel polymer electrolyte
3 composed of polymer and an organic electrolyte solution dissolving
4 lithium salt.

1 7. A lithium polymer secondary battery of claim 1,
2 wherein ceramic is contained in the polymer electrolyte.

1 8. A lithium polymer secondary battery of claim 7,

-32-

2 wherein the ceramic is at least one type selected from the group
3 consisting of Al_2O_3 , SiO_2 , ZrO_2 , MgO , and Na_2O .

1 9. A lithium polymer secondary battery of claim 7,
2 wherein the ceramic is granular, and the particle size is 10 microns
3 or less.

1 10. A lithium polymer secondary battery of claim 7,
2 wherein a polymer electrolyte is contained in at least one of the
3 positive electrode and negative electrode.

1 11. A lithium polymer secondary battery of claim 7,
2 wherein the polymer electrolyte is a gel polymer electrolyte
3 composed of polymer and an organic electrolyte solution dissolving
4 lithium salt.

1 12. A lithium polymer secondary battery comprising a
2 positive electrode and a negative electrode for occluding and
3 releasing lithium, and a polymer electrolyte, wherein the polymer
4 electrolyte is a gel polymer electrolyte containing Al_2O_3 particles
5 with particle size of 10 microns or less and 80 parts by weight or
6 less of nonaqueous electrolyte solution, and the negative electrode
7 is mixed with said gel polymer electrolyte so that Al_2O_3 particles
8 are contained.

1 13. A lithium ion secondary battery mainly comprising
2 a positive electrode using lithium transition metal compound oxide
3 as active substance, a negative electrode containing at least one
4 active substance selected from the group consisting of lithium
5 occluding and releasing carbon, metal oxide and polymer, and an
6 organic electrolyte solution, wherein the negative electrode
7 contains ceramic not relating to charge and discharge reaction of

Accepted for Publication

-34-

Abstract of the Disclosure

A lithium secondary battery has high capacity and excellent current characteristics. The lithium battery comprises of a positive electrode, a negative electrode and an electrolyte; a least
5 one of the electrodes contains ceramics particles such as Al_2O_3 irresponsible for the charge ad discharge reactions of the battery. The presence of the ceramics particles in the electrode leads to a decrease in the internal resistance of the battery because of the enhancement of ion conductivity in the electrode, resulting in
10 higher capacity at high rate discharge of the lithium secondary battery.

20140401 14:00:00

Fig 1

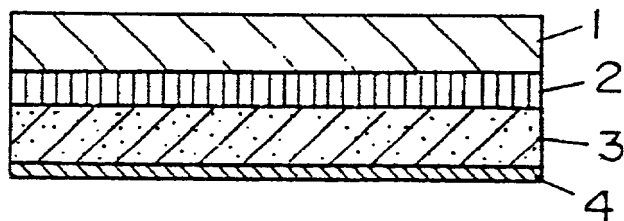


Fig 2

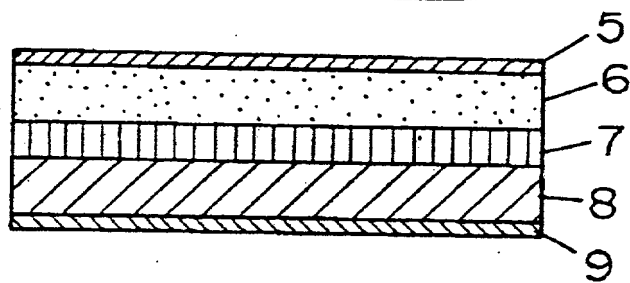


Fig 3

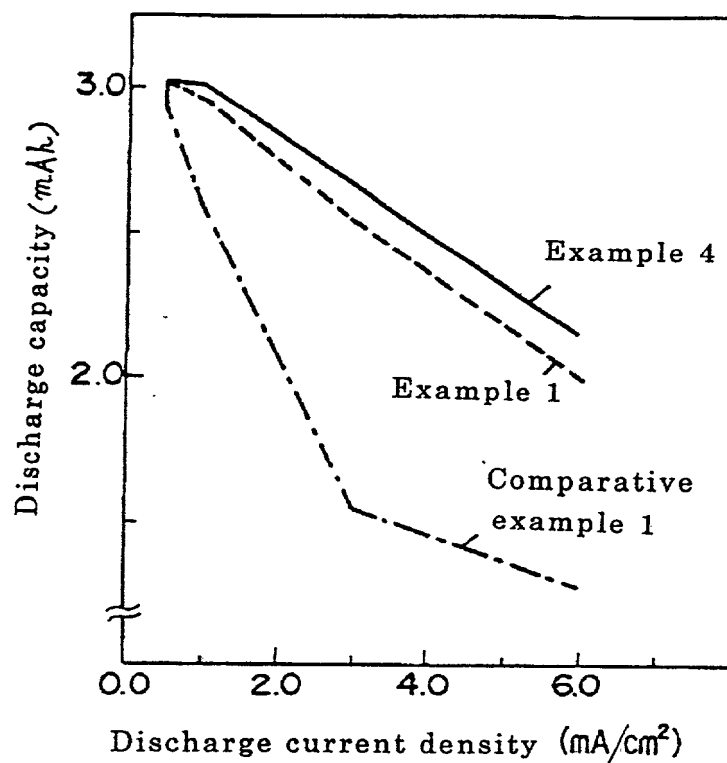


Fig 4

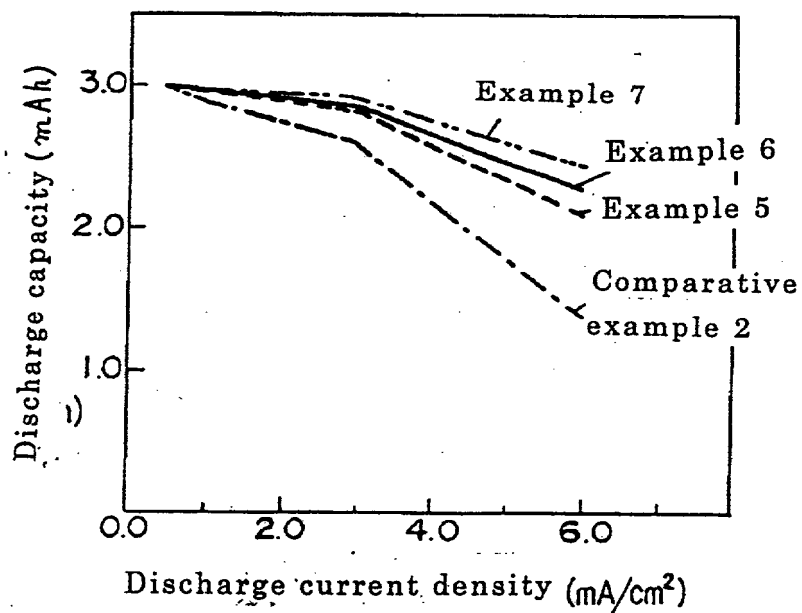


Fig 5

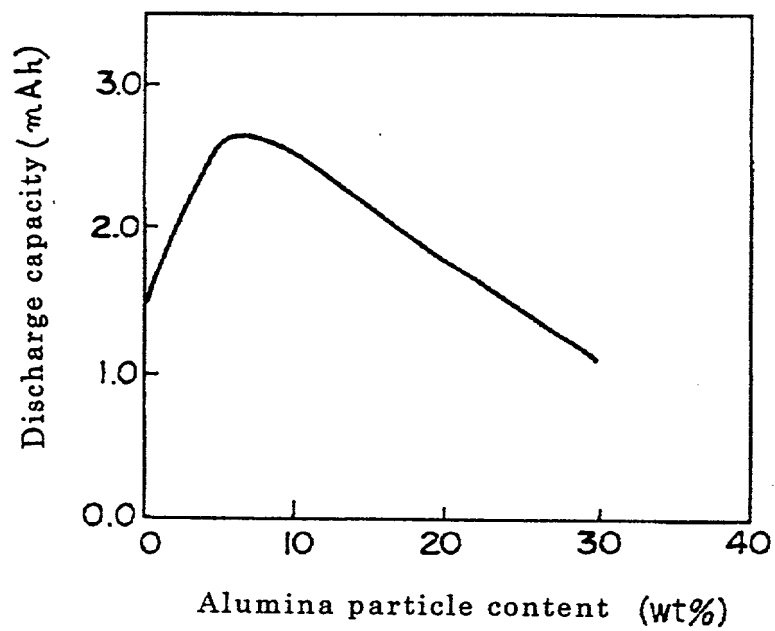


Fig 6

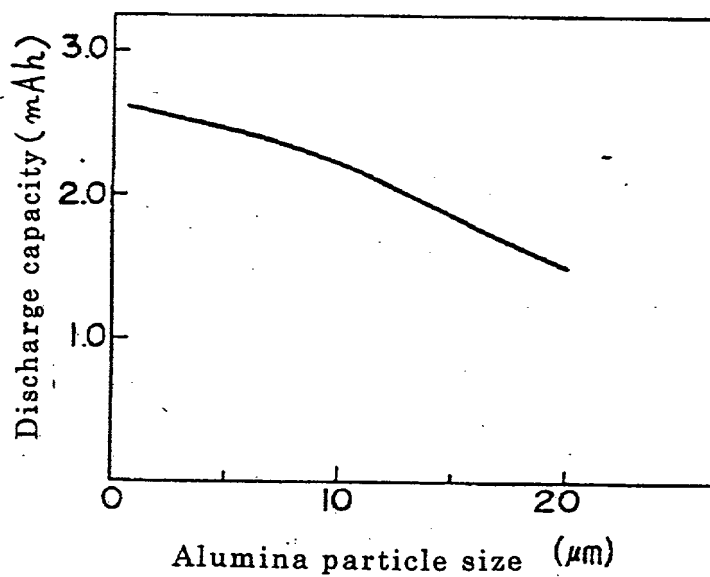


Fig 8

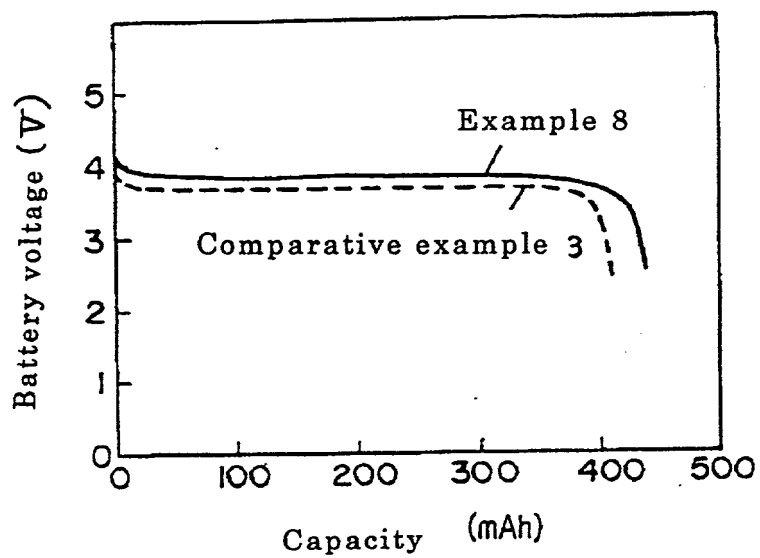


Fig 9

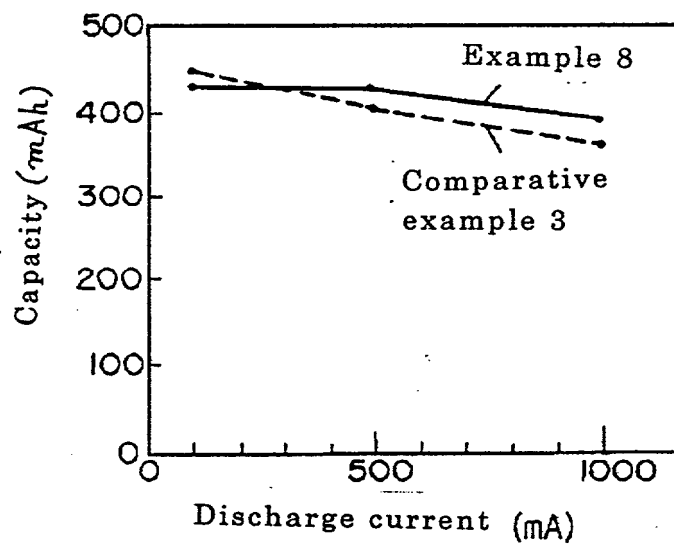
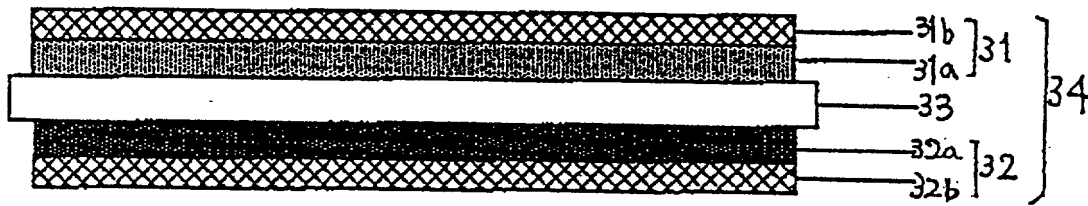
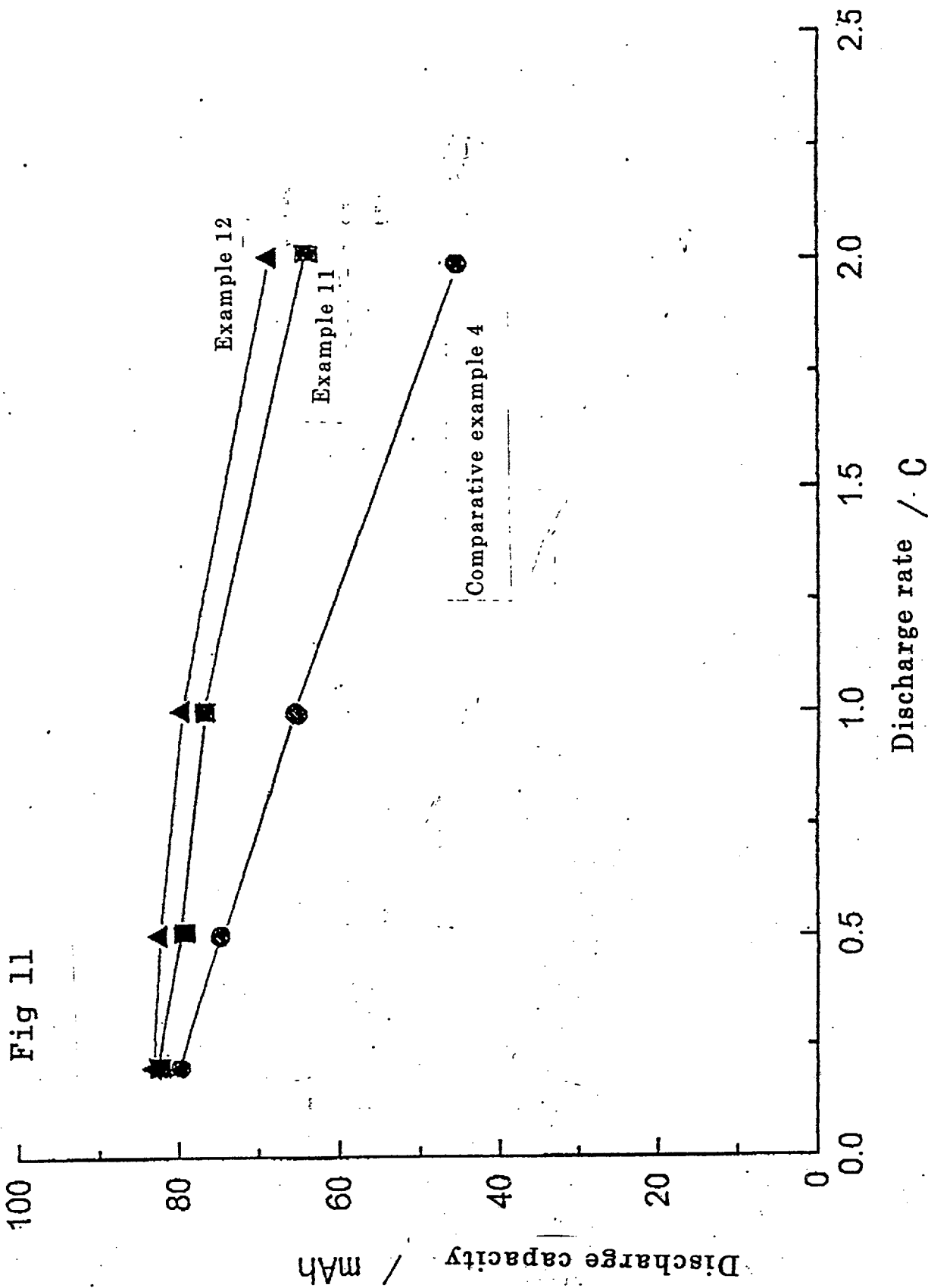


Fig 10



2025 RELEASE UNDER E.O. 14176

Fig 11



Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
LITHIUM SECONDARY BATTERY,

the specification of which is attached hereto unless the following box is checked:

☐ was filed on _____ as
United States Application Number or PCT International Application Number _____
and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Not Claimed
<u>9-58941</u>	<u>Japan</u>	<u>13 March 1997</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u>9-58964</u>	<u>Japan</u>	<u>13 March 1997</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

(Application Number) (Filing Date)

(Application Number) (Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Number)_____
(Filing Date)_____
(Status - patented, pending, abandoned)_____
(Application Number)_____
(Filing Date)_____
(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Paul F. Prestia	Reg.No. 23,031	Robert L. Andersen	Reg.No. 25,771	Rocco L. Adornato	Reg.No. 40,480
Allan Ratner	Reg.No. 19,717	Lawrence E. Ashery	Reg.No. 34,515	Jacques L. Etkowicz	Reg. No. P41,738
Andrew L. Ney	Reg.No. 20,300	Christopher R. Lewis	Reg.No. 36,201	Eric A. Dichter	Reg.No. P41,708
Kenneth N. Nigon	Reg.No. 31,549	Steven E. Koffs	Reg.No. 37,163	Mark J. Marcelli	Reg.No. 36,593
Kevin R. Casey	Reg.No. 32,117	Allan M. Wheatcraft	Reg. No. 36,307		
Benjamin E. Leace	Reg.No. 33,412	Louis W. Beardell, Jr.	Reg.No. 40,506		
James C. Simmons	Reg.No. 24,842	Ian M. Hughes	Reg.No. 41,083		

Address all correspondence to: Lawrence E. Ashery

Ratner & Prestia, Suite 301, One Westlakes, Berwyn, P.O. Box 980, Valley Forge, PA 19482-0980

Address all telephone calls to: Lawrence E. Ashery at (610) 407-0700.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor (given name, family name) Akiko Ishida

Inventor's signature _____ Date _____

Residence 1-24-11, Saigodori, Moriguchi-shi, Osaka, 570 Japan

Citizenship Japanese

Post Office Address 1-24-11, Saigodori, Moriguchi-shi, Osaka, 570 Japan

Full name of second joint inventor, if any (given name, family name) Ken Nishimura

Second Inventor's signature _____ Date _____

Residence 5-22-13, Touda-cho, Moriguchi-shi, Osaka, 570 Japan

Citizenship Japanese

Post Office Address 5-22-13, Touda-cho, Moriguchi-shi, Osaka, 570 Japan



Additional inventors are being named on separately numbered sheets attached hereto.

Full name of third joint inventor, if any (given name, family name) Masahiko Ogawa

Third inventor's signature _____ Date _____

Residence 3-5-13-201, Takatsukasa, Takarazuka-shi, Hyogo, 665 Japan

Citizenship Japanese

Post Office Address 3-5-13-201, Takatsukasa, Takarazuka-shi, Hyogo, 665 Japan

Full name of fourth joint inventor, if any (given name, family name) Nobuo Eda

Fourth inventor's signature _____ Date _____

Residence 4-3-12, Nagaodai, Hirakata-shi, Osaka, 573-01 Japan

Citizenship Japanese

Post Office Address 4-3-12, Nagaodai, Hirakata-shi, Osaka, 573-01 Japan

Full name of fifth joint inventor, if any (given name, family name) Masaki Kitagawa

Fifth inventor's signature _____ Date _____

Residence 1-34-12, Mukaida, Katano-shi, Osaka, 576 Japan

Citizenship Japanese

Post Office Address 1-34-12, Mukaida, Katano-shi, Osaka, 576 Japan

Full name of sixth joint inventor, if any (given name, family name) Tetsuhisa Sakai

Sixth inventor's signature _____ Date _____

Residence 1-16-22, Kikusuidori, Moriguchi-shi, Osaka, 570 Japan

Citizenship Japanese

Post Office Address 1-16-22, Kikusuidori, Moriguchi-shi, Osaka, 570 Japan

Full name of seventh joint inventor, if any (given name, family name) _____

Seventh inventor's signature _____ Date _____

Residence _____

Citizenship _____

Post Office Address _____